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Effect of thermal annealing on physical properties of vacuum evaporated In_2S_3 buffer layer for eco-friendly photovoltaic applications

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ABSTRACT

The present communication reports the effect of thermal annealing on the physical properties of In_2S_3 thin films for eco-friendly buffer layer photovoltaic applications. The thin films of thickness 150 nm were deposited on glass and indium tin oxide (ITO) coated glass substrates employing thermal vacuum evaporation technique followed by post-deposition thermal annealing in air atmosphere within a low temperature range 150–450 °C. These as-deposited and annealed films were subjected to the X-ray diffraction (XRD), UV-Vis spectrophotometer, current–voltage tests and scanning electron microscopy (SEM) for structural, optical, electrical and surface morphological analysis respectively. The compositional analysis of as-deposited film is also carried out using energy dispersive spectroscopy (EDS). The XRD patterns reveal that the as-deposited and annealed films ($\leq$300 °C) have amorphous nature while films annealed at 450 °C show tetragonal phase of β-In_2S_3 with preferred orientation (1 0 9) and polycrystalline in nature. The crystallographic parameters like lattice constant, inter-planner spacing, grain size, internal strain, dislocation density and number of crystallites per unit area are calculated for thermally annealed (450 °C) thin films. The optical band gap was found in the range 2.84–3.04 eV and observed to increase with annealing temperature. The current–voltage characteristics show that the as-deposited and annealed films exhibit linear ohmic behavior. The SEM studies show that the as-deposited and annealed films are uniform, homogeneous and free from crystal defects and voids. The grains in the thin films are similar in size, densely packed and observed to increase with thermal annealing. The experimental results reveal that the thermal annealing play significant role on the structural, optical, electrical and morphological properties of deposited In_2S_3 thin films and may be used as cadmium-free eco-friendly buffer layer for thin films solar cells applications.

1. Introduction

In last few years, the thin film solar cells based on heterojuntions using CdS thin film as window layer have been paid more attention due to their promising conversion efficiencies, but the growth of CdS window layer in large area production of thin film solar cells has serious

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environmental problems owing to great amount of cadmium containing waste and the utilization of ammonia in the deposition process [1,2]. The eco-friendly cadmium-free alternative buffer layers are yet to match the efficiency of thin film solar cell with CdS buffer layer and the reported world-record efficiency of CIGS solar cells with Cd-based as well as Cd-free buffer layers is found to be 21.7% and 19.7%, respectively [3]. The research work concerned to replace CdS buffer layer by other nontoxic low-absorbing materials is under progress. A number of compound semiconducting materials like In_2S_3, In_2Se_3, $InZnSe_x$, ZnO, ZnS, ZnSe are studied as a substitute to the traditional CdS buffer layer [4]. Among these, indium sulfide (In_2S_3) is an important semiconductor material for optoelectronic and photovoltaic applications due to its chemical stability, wider optical band gap (2.0–2.75 eV), photoconductive behavior, high optical transmittance ($>80\%$) and controllable electrical properties [5–7]. It is a compound semiconductor of III–VI group and exits in three crystallographic forms in nature α-In_2S_3 (cubic structure, stable upto 693 K), β-In_2S_3 (spinel structure, stable upto 1027 K) and γ-In_2S_3 (layered structure, stable above 1027 K). The β-In_2S_3 is found in most stable form at temperature below 673 K with tetragonal structure and a non toxic compound as well as exhibits n-type electrical conductivity. The internal strain affects the crystal structure of In_2S_3 thin films due to thermal expansion mismatch between film and substrate surface, variation in inter-atomic spacing and recrystallization processes [8–11]. It has potential applications to manufacture the picture tubes of color television and fabrication of green as well as red phosphors [12]. The In_2S_3 thin films can be used as window and buffer layers in heterojunction solar cells due to wide optical energy band gap and eliminating the toxicity of cadmium. So, In_2S_3 films is a most promising replacement for cadmium sulfide in Cu(In,Ga)Se_2 (CIGS) based photovoltaic cells and optical buffer layer in solar cells such as In_2S_3/$CuInX_2$ (S, Se) because it prevents health risks to operators and also decreases environmental pollution [2,10,13].

The In_2S_3 thin films can be prepared using a number of physical and chemical deposition techniques such as atomic layer deposition, chemical bath deposition, magnetron sputtering, thermal evaporation, close-spaced evaporation, spray pyrolysis, ion layer gas reaction, modulated flux deposition and wet chemical method etc [14–22]. Among these techniques, thermal vacuum evaporation is one of the most promising deposition technique and has a number of advantages like most productive, very high deposition rate, low material consumption and low cost of operation.

Calderon et al. [23] fabricated $CuInS_2$ thin film solar cell with structures Mo/$CuInS_2$/ZnS/ZnO and Mo/$CuInS_2$/In_2S_3/ZnO using ZnS and In_2S_3 as buffer layers and concluded that the former structure have best efficiency of 7.8% as compared to later structure's efficiency of 6.5%. The effect of sulfurization temperature and time on the optical, electrical and photoelectrical properties of β-In_2S_3 thin films is investigated by Yoosuf et al. [24] employing two-stage process with rapid heating in H_2S atmosphere. They found that the films have n-type conductivity and optical band gap was increased with sulfurization temperature and time. The role of chlorine doping on the opto-electronic properties of spray pyrolysed β-In_2S_3 thin films is studied by Cherian et al. [25] who observed that the photosensitivity and crystallinity were increased with optimum chlorine doping. Meng et al. [26] reported the single phase cubic structure of chemical bath deposited nanostructured indium sulfide thin films. Yahmadi et al. [27] investigated that the crystallinity of the indium sulfide thin films was strongly affected by the annealing treatment and deposition parameters like deposition time, pH-solution and thioacetamide. A study of electrochemically deposited In_2S_3 thin films is undertaken by Mari et al. [28] and found that the films have tetragonal phase in the absence of oxide. They also concluded that these films may be applied onto $CISe_2$ substrates for performance measurement of a solar cell. Hsiao et al. [29] reported n-type In_2S_3 nanoflake based thin films and observed a unique cross-linked network structure and optical band gap was found to be 2.5 eV. The tetragonal structure of β-In_2S_3 is reported by Sall et al. [30] and they concluded that the crystallinity was improved with substrate temperature. They also observed that the surface roughness decreased with temperature. Recently, the effect of film thickness on physical properties of In_2S_3 thin films is reported by Chander et al. [31] employing thermal evaporation technique. They found that the films have amorphous nature and optical band gap decreased with film thickness. So, the physical and chemical properties of the films are strongly dependent upon the deposition techniques, film thickness, annealing treatment, substrate, doping and substrate temperature. The annealing treatment may be undertaken in vacuum, air and gaseous medium like Ar, N_2, H_2 etc. Generally, the post-deposition annealing treatment is used to improve structural and optoelectronic properties, therefore, studies concerning the effect of annealing on physical properties are very important which play a significant role in efficiency improvement of optoelecronic devices. The suitable thickness for In_2S_3 thin film as buffer layer lies in the range 50–150 nm and the study on post-deposition thermal annealing treatment of these films as buffer layer is still pending.

Thorough literature survey reveals that there is a need to study non-toxic In_2S_3 thin films to use it as buffer layer in eco-friendly solar cell applications, therefore, a study on post-deposition thermal annealing treatment on the physical properties of In_2S_3 thin films is undertaken in this paper. The thin films of thickness 150 nm were deposited on glass and ITO coated glass substrates employing thermal vacuum evaporation deposition technique. These as-deposited films were subjected to thermal annealing in air atmosphere within temperature range 150–450 °C. The physical properties of these as-deposited and annealed films have been carried out employing X-ray diffraction, UV–vis spectrophotometer, current–voltage tests and scanning electron microscopy. The compositional analysis of as-deposited film is also undertaken using EDS. The crystallographic parameters are calculated for thermally annealed (450 °C) thin films. The optical parameters like extinction coefficient, optical energy band gap, absorption coefficient and refractive index of as-deposited and annealed films are also calculated.